Reactions of Transition-Metal σ-Acetylide Complexes. 1. The Reaction between $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ and Tetracyanoethylene: X-ray Structure of $\mathrm{W(CO)_2[\eta^3\text{-}C(CN)CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4}$

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The reaction between $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ and $\mathrm{C_2(CN)_4}$ gives a relatively long-lived (hours) green paramagnetic compound (nine-line ESR spectrum, $g = 1.997$). On standing the σ-cyclobutenyl complex $\mathrm{W[\overline{C{=}CPhC(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)}$ is obtained, which is slowly converted to the σ-butadienyl derivative $\mathrm{W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)}$. UV irradiation of the butadienyl complex gives the dicarbonyl $\mathrm{W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)}$ in which the cyanocarbon ligand has been shown crystallographically to be best represented either as a methylenetungstabicyclobutane or as a localized en–yl system, probably with substantial back-bonding from the metal to the σ-bonded carbon. Crystals are monoclinic of space group $P2_1/n$ with $a = 12.194$ (4) Å, $b = 20.858$ (5) Å, $c = 8.969$ (2) Å, $\beta = 98.21$ (2)°, and $Z = 4$; the unit cell also contains two molecules of $\mathrm{C_2(CN)_4}$. Refinement of 2781 data converged with $R = 0.0389$ and $R_w = 0.0384$. The structural data are used to rationalize unusual ^{13}C chemical shifts of the metal-bonded carbon atoms.

Introduction

The migratory insertion reaction is a characteristic feature of the chemistry of the M–C(sp^3) bond in transition-metal complexes, but its occurrence with M–C(sp^2) and M–C(sp) bonds is by no means as widespread.[1] In the particular case of metal σ-acetylide complexes $\mathrm{L_nMC{\equiv}CR}$, few well-substantiated examples are known. Thus, as far as we are aware, no case of the insertion of CO into the $\mathrm{M{-}C_2R}$ bond has been reported, although the reverse reaction, the decarbonylation of the (phenylethynyl)acyl complexes $\mathrm{M(COC_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ (M = Mo, W) to give $\mathrm{M(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$, has been described.[2]

Electrophilic olefins and alkynes are reported to insert into the $\mathrm{M{-}C_2R}$ bonds of some palladium(II) and platinum(II) complexes. Thus, reactions between tetracyanoethylene and *trans*-$\mathrm{Pt(C_2H)_2(PMe_2Ph)_2}$ or *trans*-$\mathrm{Pt(C_2Me)_2(AsMe_3)_2}$ afford the complexes *trans*-$\mathrm{Pt[C(CN)_2C(CN)_2C_2H](C_2H)(PMe_2Ph)_2}$ and *trans*-$\mathrm{Pt[C(CN)_2C(CN)_2C_2Me](C_2Me)(AsMe_3)_2}$, respectively.[3] Dimethyl acetylenedicarboxylate reacts with *trans*-$\mathrm{PdX(C_2R)(PR'_3)_2}$ (R = Et, Bu, Ph; R′ = Et, Bu; X = Cl, Br, I) to give *trans*-$\mathrm{PdX[C(CO_2Me){=}C(CO_2Me)C_2R](PR'_3)_2}$,[4] although with *trans*-$\mathrm{HM(C_2Ph)(PEt_3)_2}$ (M = Pd, Pt), the alkyne inserts into the M–H bond instead,[5] as confirmed by an X-ray structural study of *trans*-$\mathrm{Pd[C(CO_2Me){=}CH(CO_2Me)](C_2Ph)(PEt_3)_2}$ (1).[6]

The C≡C triple bond of metal acetylide complexes is susceptible to attack by electrophiles.[7] Thus, protic acids containing noncoordinating anions, or cationic alkyl reagents, may add to the β-carbon to give vinylidene complexes.[8] With HCl, addition to give α-chlorovinyl complexes may occur,[9] but in other cases the M–C bond is cleaved.[10] A key contribution to this chemistry is the study[3] of reactions of alkynylplatinum(II) complexes with aprotic substrates, which showed that in addition to the reactions mentioned above, the following types of reactions occur: (i) oxidative addition to the metal center to give platinum(IV) alkynyl compounds, for example, with $\mathrm{I_2}$, MeI, or $\mathrm{CF_3I}$, (ii) formation of a 1:1 π-complex, as found with $\mathrm{(CF_3)_2CO}$, (iii) insertion into the C–H bond of an ethynyl complex, illustrated by the formation of *trans*-$\mathrm{Pt[C_2C(OH)(CF_3)_2]_2(PMe_2Ph)_2}$ from $\mathrm{(CF_3)_2CO}$ and *trans*-$\mathrm{Pt(C_2H)_2(PMe_2Ph)_2}$, and (iv) attack at the C≡C triple bond to give vinylplatinum(II) compounds. An unusual example of the latter reaction is addition of $\mathrm{CF_3COCl}$ to *trans*-$\mathrm{Pt(C_2Me)_2(AsMe_3)_2}$ to form the vinyl ketone complex *trans*-$\mathrm{Pt[CCl{=}CMeC(O)CF_3]_2(AsMe_3)_2}$.

Cycloadditions of several substrates to the C≡C bond in metal σ-acetylide complexes have been described by several workers. Diphenylketene and the corresponding phenylethynyl complex affords the cyclobut-1-en-3-onyl derivatives $\mathrm{M[C{=}CPhC(O)CPh_2]L_n}$ (2, $\mathrm{ML_n}$ = $\mathrm{Fe(CO)(L')(\eta\text{-}C_5H_5)}$, L′ = CO, $\mathrm{PPh_3}$; $\mathrm{Ni(PPh_3)(\eta\text{-}C_5H_5)}$],[11] and hexafluoroacetone gives 1:1 adducts (3) with $\mathrm{Fe(C_2Ph)(CO)(L)(\eta\text{-}C_5H_5)}$ (L = CO, $\mathrm{PPh_3}$) and a 1:2 adduct (4) with the dicarbonyl.[12] The same workers also studied the reactions of these complexes with tetracyanoethylene. In $\mathrm{CH_2Cl_2}$, the cyclobutenyl complex $\mathrm{Fe[\overline{C{=}CPhC(CN)_2C}(CN)_2](CO)_2(\eta\text{-}C_5H_5)}$ (5) is obtained from $\mathrm{Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)}$, but in diethyl ether, the initial formation of a green charge-transfer complex is followed by the precipitation of a zwitterionic intermediate, formulated as $\mathrm{Fe[C^+{=}CPhC(CN)_2C^-(CN)_2](CO)_2(\eta\text{-}C_5H_5)}$ (6), which

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(1) For reviews, see F. Calderazzo, *Angew. Chem.*, **89**, 305 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 299 (1977); A. Wojcicki, *Adv. Organomet. Chem.*, **11**, 87 (1973).

(2) A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, and N. A. Ustynyuk, *Izv. Akad. Nauk SSSR*, **1978**, 2375.

(3) M. H. Chisholm and L. A. Rankel, *Inorg. Chem.*, **16**, 2177 (1977).

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(8) For a review, see M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, **22**, 59 (1983).

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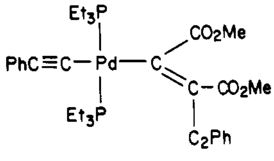
slowly cyclizes to the cyclobutenyl complex. In the case of $\mathrm{Fe(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)}$, the isolated product is apparently a 7:3 mixture of the corresponding zwitterionic and cyclobutenyl complexes.



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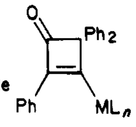

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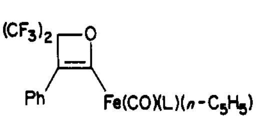

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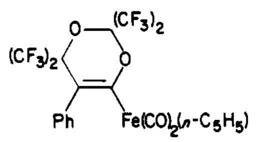

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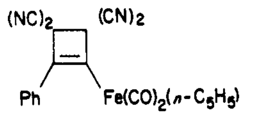

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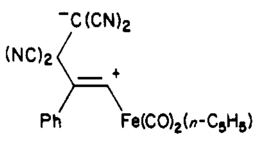

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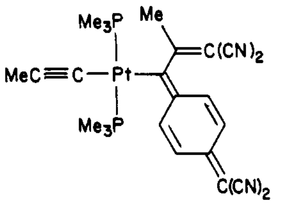

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Yet another type of reaction is that occurring between 7,7,8,8-tetracyanoquinodimethane and *trans*-$\mathrm{Pt(C_2R)_2(PR'_3)_2}$ (R = H, Me; R′ = Me, Et) from which stable purple-black 1:1 adducts were isolated;[13] the X-ray structure of one of these (**7**) showed that addition of the cyanocarbon to a propynyl group was followed by rearrangement to form the 1-(4-(dicyanomethylene)cyclohexa-2,5-dien-1-ylidene)-3,3-dicyano-2-methylprop-2-en-1-yl ligand.[14]

At the time that the communication describing the $\mathrm{Fe(C_2Ph)(CO)(L)(\eta\text{-}C_5H_5)/C_2(CN)_4}$ system[12] appeared, we had studied the reaction between this cyanoolefin and the readily available complex $\mathrm{Ru(C_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}$. The product from this reaction contained only one $\mathrm{PPh_3}$ molecule, and the ligand formed by addition of $\mathrm{C_2(CN)_4}$ to the $\mathrm{C_2Ph}$ residue was shown to be the η^3-$\mathrm{C(CN)_2CPhC{=}C(CN)_2}$ group, which was readily converted to an η^1-butadienyl system by addition of a two-electron-donor ligand to the metal center.[15] These studies are fully reported in the following paper[16] but are more readily understood in the light of results obtained with the $\mathrm{C_2(CN)_4/W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ system, which are described below. Some of these results have been communicated briefly.[17]

Results and Discussion

The reaction between $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ (**8**; Scheme I) and $\mathrm{C_2(CN)_4}$ in benzene results in the immediate formation of an intensely green-colored solution. In dichloromethane, on the other hand, yellow crystals are obtained, which have been shown to be the cyclobutenyl complex, $\mathrm{W[\overline{C{=}CPhC(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)}$ (**9**) by an X-ray crystallographic study.[17] If a solution of **9** in $\mathrm{CDCl_3}$ is allowed to stand, the ^{1}H NMR spectrum changes over a period of 24 h. At the end of this time, the butadienyl complex **10** is present; the same complex was obtained from a reaction between **8** and $\mathrm{C_2(CN)_4}$ after 2 days. UV irradiation of **10** results in loss of one CO to give $\mathrm{W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)}$ (**11**). Compound **11**, whose identity was confirmed by the single-crystal X-ray study described below, is also a minor product as a $\mathrm{0.5C_2(CN)_4}$ solvate from the reaction affording **10**. These reactions are summarized in Scheme I.

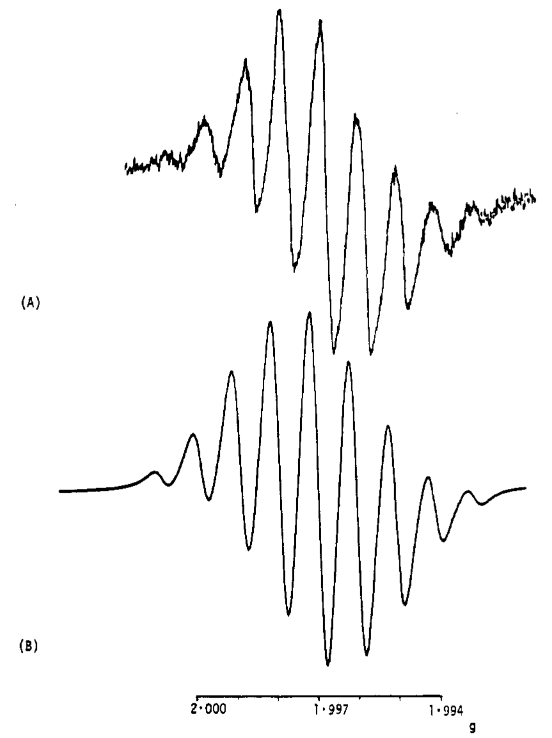
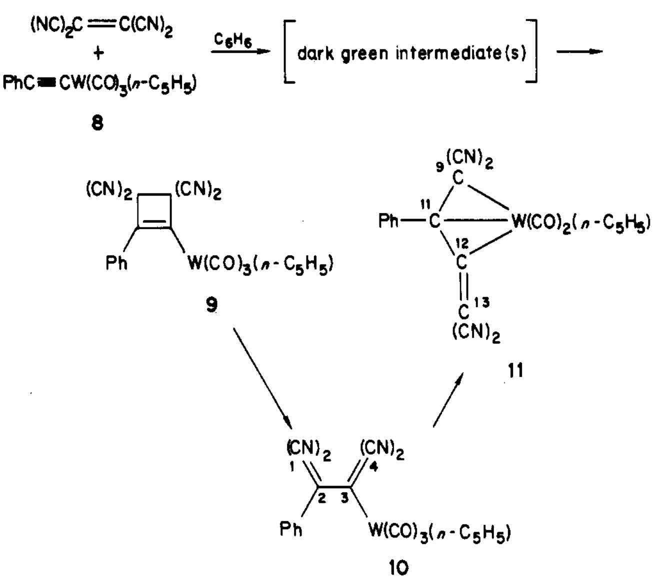


Figure 1. (A) ESR spectrum of an equimolar mixture of $\mathrm{C_2(CN)_4}$ and $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ in benzene, immediately after mixing. (B) Simulated spectrum of an electron coupled equally to four nitrogen atoms (a_N = 1.59 G).

Scheme I



The green benzene solution obtained immediately after mixing **8** and $\mathrm{C_2(CN)_4}$ contains a paramagnetic compound, presumably formed by oxidation of **8** by the cyanoolefin. Although the formation of $\mathrm{[C_2(CN)_4]^{-\cdot}}$ by alkali-metal reduction of tetracyanoethylene is well established, it was

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[13] H. Masai, K. Sonogashira, and N. Hagihara, *J. Organomet. Chem.*, **34**, 397 (1972).

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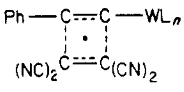
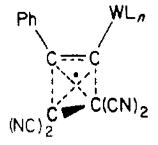
[16] M. I. Bruce, T. W. Hambley, M. R. Snow, and A. G. Swincer, following paper in this issue.

[17] M. I. Bruce, T. W. Hambley, M. R. Snow, and A. G. Swincer, *J. Organomet. Chem.*, **226**, C1 (1982).

quickly shown that our product differs from this yellow radical anion.[18] The ESR spectrum of the green compound is shown in Figure 1. The nine-line spectrum (g = 1.997) can be simulated by assuming that the unpaired electron is coupled equally to four nitrogen atoms (a_N = 1.59 G, line width = 0.73 G), as found for $[C_2(CN)_4]^{-}\cdot$ (g = 2.0026). No coupling with ^{13}C or ^{183}W was observed. We have not been able to characterize this species further at this stage, but a structure in which the $C_2(CN)_4$ interacts in symmetrical fashion with the acetylide ligand, either in a planar A or tetrahedral B four-center arrangement, is possible.



A



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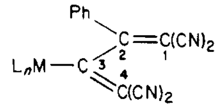
The ESR-active species decays over a period of several hours, the color of the solution lightening to yellow; complex **9** can be isolated from this solution and can also be obtained directly from the two reactants in CH_2Cl_2 solution. Microanalytical and mass spectrometric data showed that **9** is a 1:1 adduct of **8** and $C_2(CN)_4$, and we have previously reported[17] the crystallographic characterization of this compound as the cyclobutenyl derivative **9**. In solution, its spectroscopic properties are consistent with the solid state structure: the IR spectrum contains a ν(CN) band at 2244 cm^{-1}, ν(CO) bands characteristic of the $W(CO)_3$ group at 2046, 1983, and 1974 cm^{-1}, and a ν(C=C) band at 1489 cm^{-1}. In the ^1H NMR spectrum, the expected resonances at δ 6.16 (C_5H_5) and 7.64 (Ph) are present, while the ^{13}C NMR spectrum contained resonances at δ 94.0 (C_5H_5), 112.2, and 113.2 (CN), four between δ 127 and 132 (Ph), and δ 216.7 (CO). Resonances for the other carbons could not be detected before conversion to **10** occurred.

The molecular structure of **9** is notable for the relatively long C–C bond [1.60 (1) Å] on the opposite side of the C_4 ring to the double bond. This is the bond which is cleaved in the formation of the orange butadienyl complex **10**. In solution, this facile isomerization is complete within hours at ambient temperatures. The characterization of **10** is supported by microanalytical data and mass spectrometry, which confirm that **10** is also a 1:1 adduct of **8** and $C_2(CN)_4$, isomeric with **9**, from which it is distinguished by its spectroscopic properties. The IR spectrum contains two medium intensity ν(CN) bands at 2222 and 2210 cm^{-1}, ν(CO) bands at 2046 and 1981 cm^{-1}, and a band assigned to ν(C=C) at 1522 cm^{-1}. The ν(CN) and ν(C=C) frequencies are similar to those found for crystallographically characterized ruthenium–butadienyl complexes,[15,16] and this structural assignment for **10** is further confirmed by the NMR spectra.

During the isomerization of **9**, signals at δ 5.9 (C_5H_5) and 7.8 (Ph) in the ^1H NMR spectrum grow at the expense of the resonances of **9**. In the ^{13}C NMR spectrum (Table I) signals for C_5H_5 (δ 95.7), CN (four between δ 113 and 116), Ph (four between δ 130 and 135), and CO (δ 196.9, 216.8, 217.8) are accompanied by four resonances at δ 77.4, 99.8, 182.8, and 221.7 for the C_4 skeleton of the butadienyl group [C(1), C(4), C(2), and C(3), respectively]. These assignments are fully discussed elsewhere[16] and are substantiated by comparisons with the spectrum of $[Fe\{CH{=}C(CN)_2\}(CO)_4]^-$, in which the α- and β-carbons are found at δ 228.2 and 93.9, respectively.[19] The low-field chemical shift of the metal-bonded carbons in these complexes is of interest, suggesting that there is considerable electron deficiency in this region of the molecule.

Table I. ^{13}C Chemical Shifts for Some Butadienyl Complexes



ML_n	chemical shift (δ) C(1)	C(2)	C(3)	C(4)
$W(CO)_3(\eta\text{-}C_5H_5)$[a]	77.4	182.8	221.7	99.8
$Ru(CN\text{-}t\text{-}Bu)_2(\eta\text{-}C_5H_5)$[b]	69.3	179.7	226.2	90.8
$Ru(dppe)(\eta\text{-}C_5H_5)$[b]	73.9	181.9	225.7	95.1
$Fe(CO)_2(\eta\text{-}C_5H_5)$[c]	74.9	181.2	215.1	98.0

[a] This work. [b] Reference 19. [c] M. I. Bruce and A. G. Swincer, unpublished work.

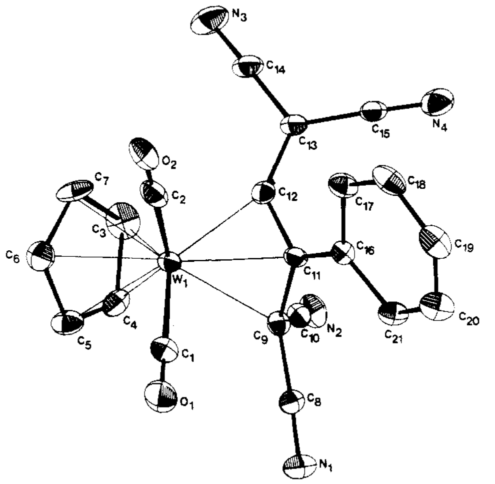


Figure 2. ORTEP plot of $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)$ (**11**), showing atom numbering scheme.

The three CO resonances observed for the $W(CO)_3$ group reflect the asymmetry of the butadienyl group which is a feature of the solid-state structures of analogous ruthenium complexes.[15,16] The diene skeleton is nonplanar with localized C—C single and C=C double bonds and is probably sufficiently bulky to hinder rotation so that it is impossible for the three CO groups to become equivalent.

The third complex **11** isolated from the reaction between **8** and $C_2(CN)_4$, which is best prepared by UV irradiation of **10**, is formed by simple loss of CO from **10** and concomitant coordination of the C(1)–C(2) portion of the butadienyl group. Complex **11** was identified by microanalysis and mass spectrometry and from its IR spectrum, which contains a characteristic two-band ν(CO) absorption at 2080 and 2025 cm^{-1}, two ν(CN) bands at 2232 and 2222 cm^{-1}, and a ν(C=C) band at 1586 cm^{-1}. In the ^1H NMR spectrum, the C_5H_5 and Ph resonances occur at δ 5.9 and 7.5, respectively, while in the ^{13}C NMR spectrum, the C_5H_5, CN, and Ph resonances are found at δ 94.1, between δ 112.2 and 118.4, and between δ 128.7 and 131.5, respectively; the two CO ligands give signals at δ 201.1 and 203.8. Only three of the four resonances expected for the C_4 skeleton were found, at δ 4.7 [C(11)], 79.4 [C(9)], and 206.6 [C(12)]. Again, these assignments are discussed in our account of some related ruthenium chemistry.[16]

The molecular geometry of **11** was fully delineated by a single-crystal X-ray structure. The unit cell of **11** con-

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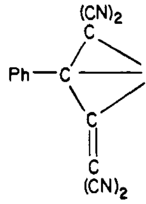
(18) W. D. Phillips, J. C. Powell, and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960).

(19) T. Mitsudo, H. Watanabe, Y. Watanabe, N. Nitani, and Y. Takegami, *J. Chem. Soc., Dalton Trans.*, 395 (1979).

tains four symmetry-related discrete molecules in general sites, together with two molecules of $C_2(CN)_4$ lying at centers of symmetry. Figure 2 is an ORTEP plot[20] of a molecule of **11** and shows the atom numbering scheme. The geometry of the tetracyanoethylene "solvate" molecule is similar to that found in the monoclinic[21] and cubic[22] forms of the cyannolefin [C≡N = 1.13 (1), C—CN = 1.464 (15) Å] with the exception of the C=C separation [1.243 (18) Å], which appears to be somewhat shorter, even allowing for the large esd. We have no explanation for this anomaly.[23]

The tungsten atom is bonded to two CO groups [W–C = 2.016, 2.048 (8) Å], the cyclopentadienyl ligand [W–C(av) = 2.304 Å], and the cyanocarbon ligand, of which three carbons are within normal bonding distance. The best description of the WC_3 unit is related to the tungstacyclobutadiene complexes described recently.[24] Thus we may consider the representation as a methylenetungstabicyclobutane derivative (C). In accord with this formulation are the short W–C bonds W–C(9) [2.285 (8) Å], W–C(11) [2.253 (7) Å], and W–C(12) [2.075 (8) Å], together with the C(9)–C(11) [1.480 (9) Å] and C(11)–C(12) [1.439 (9) Å] separations. The dihedral W–C(12)–C(11)/W–C-(9)–C(11) is 116.6°, while the angle C(9)C(11)C(12) is 104.5 (6)°. Theoretical studies of metallacyclobutadiene complexes[25a] have shown the possibility of the W d_π orbitals interacting with suitable orbitals (b_2 and a_2) of the $[C_3H_3]^{3-}$ fragment in a planar WC_3H_3 fragment. In the present case, we envisage that the W d_π orbitals could overlap with the π orbitals of the $C{=}C(CN)_2$ fragment and the sp^3 orbital on C(11) to give a structure which is less stable than the metallacyclobutadiene (see below). Attachment of C(9) and C(12) to W is considered to be analogous to that in metallacyclobutanes.[25b]



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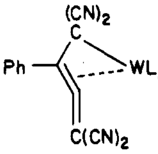

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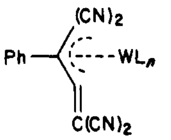
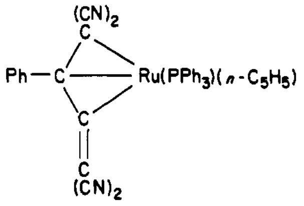


E

The chemical stability of metallacyclobutadienes has given cause for remark. No such stability is found in the present case, since reactions with nucleophiles (CNR, PR_3) give butadienyl complexes. Two other formulations may be considered, namely, as the η^2-allenylmethyl D or the η^3-allylic E group. Either of these must provide some explanation of the short W–C(12) distance, which may be compared with the W–CO distances mentioned above, and with the W–C(carbene) separation found in $W(CPh_2)(CO)_5$ [2.14 (2) Å].[26] There is evidently a considerable degree of back-bonding from tungsten to C(12). Other structural features supporting the allenyl description are (i) the C(9)–C(11)–C(12)–C(13) sequence, whose separations are consistent with C—C single bond, C=C double bond interacting with W, and C=C double bond, (ii) the angle C(11)–C(12)–C(13) [132.1 (7)°] which is similar to those found in η^2-allene complexes, e.g., $Pt(\eta^2\text{-}CH_2{=}C{=}CH_2)(PPh_3)_2$ [142 (3)°][27] or $[Ru(\eta^2\text{-}CH_2{=}C{=}CH_2)(PMe_3)_2(\eta\text{-}C_5H_5)]^+$ [145.2 (6)°],[28] and (iii) the near orthogonality of the two $C(CN)_2$ fragments [dihedral C(8)C(9)C(10)/C-(13)C(14)C(15) = 77.9°], an expected consequence of the orthogonality of the allene π orbitals. Asymmetry in bonding of the allene has been observed previously.[29]

The allylic formulation D, in which the dicyanomethylene fragment is attached to a terminal carbon [C-(12)] is consistent with the similarity in bond lengths C(9)–C(11) and C(11)–C(12), and the overall geometry greatly resembles that found earlier for the η^3-*trans*-2,3-bis(methoxycarbonyl)acryloyl ligand in its $Fe(CO)_3$ complex (**13**).[30] A more comprehensive description of the bonding in this and related complexes must await an MO-based treatment. We note, however, that these two structures are related by the long-established correspondence between O and $C(CN)_2$.[31]



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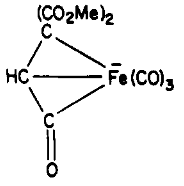

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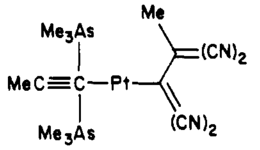

14

The structure provides an explanation for the extreme low-field ^{13}C chemical shift found for C(12) (>200 ppm). This carbon atom has some carbenic character and is electron-deficient as a result of attachment both to the metal (with associated back-bonding) and to the strongly electrophilic dicyanomethylene group. This feature further emphasizes the similarity between the cyanocarbon ligand in **11** and the η^3-acryloyl ligand mentioned above, in which the "acyl" carbon resonates at δ 235.7.[32]

Course of the Reaction. Scheme I summarizes the observations we have made in this system and provides a basis for explaining the formation of similar complexes in other systems. The first-formed product is the deep green complex, which is probably formed by oxidation of the phenylacetylide by the cyanoolefin. However, we have

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[23] A reviewer suggested that the $C_2(CN)_4$ molecule may be disordered, with an approximately ordered $(CN)_4$ skeleton and two different orientations of the C=C moiety at 90° to one another. The only peak found in the region of the C=C has intensity 0.46 e $Å^{-3}$ at 1.03 Å from C(23); further refinement gave no evidence for the proposed disorder.

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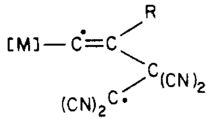
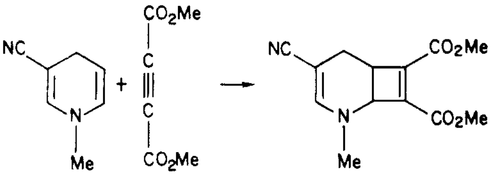
not detected the $[C_2(CN)_4]^{-\cdot}$ radical anion, so that if formed, it must add rapidly to the acetylide to give the green species; alternatively, this is formed directly by attack on the β-carbon of the acetylide moiety. The ESR spectrum gives little information concerning the structure of this compound, apart from suggesting that the unpaired electron is coupled equally to the four nitrogen nuclei. Recent theoretical calculations have shown that the two HOMO's of $Fe(C_2H)(PH_3)_2(\eta\text{-}C_5H_5)$ lie close together and are respectively 10 and 12% localized on the β-carbon, thus rationalizing the observed position of electrophilic attack on acetylides.[7] Loss of an electron from the HOMO to $C_2(CN)_4$, and C-C bond formation to give an intermediate of the type



results in an intermediate biradical where one electron would be associated with the $C_2(CN)_4$ portion, the other being in an orbital largely centered on the metal fragment. Studies of related systems in our laboratory have indicated that in some cases, more than one ESR species may be formed; these experiments will be described elsewhere.

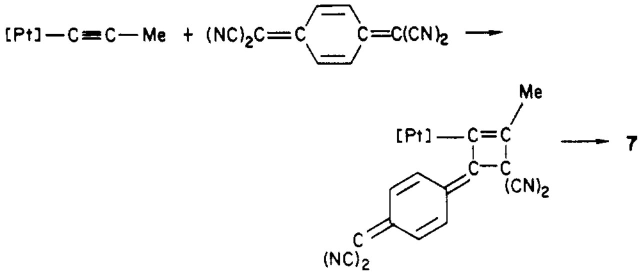
The ESR spectrum of our green compound is not consistent with any of the formulations proposed by Davison and Solar[12] in their investigation of the reactions between $Fe(C_2Ph)(CO)(L)(\eta\text{-}C_5H_5)$ (L = CO, PPh_3) and $C_2(CN)_4$, although it is likely that their green charge-transfer complex formed in diethyl ether is related to it.

The intermediacy of the green compound in the formation of cyclobutene **9** has not been demonstrated directly. Decolourization of the solution is accompanied by formation of **9**, although as described above, **9** can also be obtained (in CH_2Cl_2) from systems which do not develop any green coloration. Cycloaddition of olefins to alkynes is a [2 + 2] reaction and is formally forbidden as a concerted thermal reaction, by the principle of orbital symmetry conservation.[33] However there are many examples of such reactions in organic chemistry,[34] for example, the addition of cyanoolefins to vinyl ethers and of electrophilic alkynes to dihydropyridines.[35]



Extensive studies of such reactions have shown that they may proceed via biradical or dipolar intermediates. These extremes are found in the formation of cyclobutanes from $CCl_2{=}CF_2$[36] and in the addition of electron-rich to electron-poor olefins, respectively.[37] The reactions described herein offer an interesting contrast to the latter, in that radical species are formed at an early stage of the reaction. We note here that [2 + 2] cycloaddition of tetracyanoethylene to alkynes has not been reported previously; our reaction represents an interesting and unusual activation of the C≡C triple bond by the transition-metal substituent. The isoelectronic nature of the ligands $RC{\equiv}C^-$ and CO suggest that this activation results from back-bonding of the metal to the acetylide fragment, although the theoretical study mentioned above suggested that the acetylide ligand is essentially a pure σ donor ligand. Nevertheless, the acetylide π^* level contains 0.14-electron [in $Fe(C_2H)(CO)_2(\eta\text{-}C_5H_5)$], and the Fe–C bond length of 1.920 (6) Å in $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$[38] (sum of C(sp) and Fe radii = 1.98–2.03 Å) both indicate a degree of electron transfer from the metal to the C≡C triple-bond orbitals.

The isomerization of **9** to **10** is an example of the cyclobutene–butadiene isomerization used by Woodward and Hoffman to introduce their concepts of orbital symmetry conservation.[33] In the particular example reported here, the identical substituents (CN) at each end of the butadiene do not provide any information concerning the direction of ring opening; i.e. whether this process is conrotatory or disrotatory. We are examining related systems to see whether the usual conrotatory process is altered by the metal substituent. The reaction, which is facilitated by the long (and hence weakened) C—C bond in complex **9** is the second step in the cleavage of the C=C double bond of the tetracyanoethylene, giving a product in which formal addition of two dicyanomethylene groups, one to each carbon of the C≡C triple bond in the alkyne complex **8**, has occurred. This provides a route to the earlier described product **7** from tetracyanoquinodimethane and *trans*-$Pt(C_2R)_2(PR'_3)_2$.[13] The formation of the unusual ligand in **7** can now be seen to have occurred by initial formation of an undetected cyclobutenyl complex, which gives **7** by a ring-opening reaction similar to that found with **9**.



[Pt] = $Pt(C_2Me)(PMe_3)_2$

As mentioned earlier, the reaction between *trans*-$Pt(C_2Me)_2(AsMe_3)_2$ and $C_2(CN)_4$ is thought to give an insertion product; the IR spectrum of this complex [ν(CN) 2225, ν(C=C) 1560 cm^{-1}] is also consistent with a formulation **14**, analogous to **10**, but ^{13}C NMR or (preferably) X-ray structural data are required before the nature of this complex can be confirmed. We note that comparison of the spectra of the yellow zwitterionic and yellow-brown cyclobutenyl complexes, obtained in the $Fe(C_2Ph)(CO)(L)(\eta\text{-}C_5H_5)$ (L = CO, PPh_3)/$C_2(CN)_4$ system,[12] with those of crystallographically identified derivatives, and of the butadienyl complex **10** (Table II), strongly suggests that these two compounds should be reformulated as the cyclobutenyl and butadienyl complexes, respectively.

Finally, we make a comparison of the reactions described above, with the long-known reactions between 2-alkenyl- or 2-alkynylmetal complexes and tetracyanoethylene.[39,40] These proceed via initial formation of a dipolar interme-

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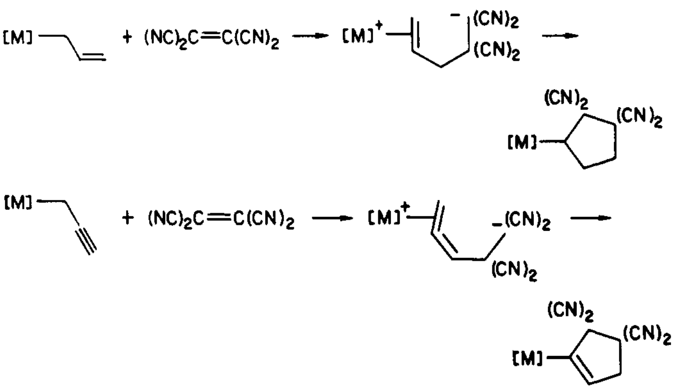
Table II. Bond Lengths (Å) in $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (11)

W(1)–C(1)	2.041 (8)	C(9)–C(11)	1.480 (9)
W(1)–C(2)	2.016 (8)	C(11)–C(12)	1.439 (9)
W(1)–C(3)	2.309 (8)	C(11)–C(16)	1.472 (9)
W(1)–C(4)	2.343 (8)	C(12)–C(13)	1.355 (10)
W(1)–C(5)	2.308 (9)	C(13)–C(14)	1.427 (11)
W(1)–C(6)	2.283 (9)	C(13)–C(15)	1.414 (11)
W(1)–C(7)	2.275 (8)	C(14)–N(3)	1.131 (12)
W(1)–C(9)	2.285 (8)	C(15)–N(4)	1.151 (12)
W(1)–C(11)	2.253 (7)		
W(1)–C(12)	2.075 (8)	C(16)–C(17)	1.407 (10)
		C(17)–C(18)	1.380 (11)
C(1)–O(1)	1.125 (10)	C(18)–C(19)	1.382 (15)
C(2)–O(2)	1.128 (11)	C(19)–C(20)	1.365 (13)
		C(20)–C(21)	1.385 (11)
C(3)–C(4)	1.417 (11)	C(21)–C(16)	1.384 (10)
C(4)–C(5)	1.372 (12)		
C(5)–C(6)	1.403 (11)	C(22)–C(23)	1.452 (14)
C(6)–C(7)	1.397 (12)	C(23)–C(24)	1.476 (15)
C(7)–C(3)	1.410 (13)	C(23)–C(23′)	1.243 (18)
		C(22)–N(5)	1.117 (11)
C(8)–C(9)	1.429 (10)	C(24)–N(6)	1.140 (12)
C(8)–N(1)	1.159 (10)		
C(9)–C(10)	1.448 (10)		
C(10)–N(2)	1.137 (11)		

diate (but without the formation of any radical species) to give a formal (3 + 2) cycloaddition product:



Interestingly, the complex $Fe(CH_2C{\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)$, which cannot form the dipolar intermediate, does not react with the cyanoolefin.[40]

Experimental Section

All reactions were conducted under a nitrogen atmosphere, manipulations involving solutions being carried out in conventional Schlenk tubes. Solvents were dried and distilled in nitrogen before use. Literature methods were used to prepare $W(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$[41] and tetracyanoethylene,[42] which was resublimed before reaction.

Instrumentation: Perkin-Elmer 457 and 683 double-grating IR spectrophotometers; Bruker WP80 NMR spectrometer (^{1}H at 80 MHz and ^{13}C at 20.1 MHz); Varian E-9 ESR spectrometer (operating at X-band frequencies); AEI-GEC MS 3074 mass spectrometer (70-eV ionizing energy and 8-kV accelerating potential).

Preparation of Tungsten Complexes. (a) $W[\overline{C{=}CPhC(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (9). A mixture of $W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$ (122 mg, 0.28 mmol) and $C_2(CN)_4$ (44 mg, 0.34 mmol) in dichloromethane (15 mL) was stirred for 45 min. Addition of EtOH to the resulting yellow solution gave yellow microcrystals of $W[\overline{C{=}CPhC(CN)_2C}(CN)_2](CO)_3(\eta\text{-}C_5H_5)$ (**9**) (120 mg, 76%): mp 108–114 °C dec; infrared (CH_2Cl_2) ν(CO) 2046 (s), 1983 (vs), 1974 (sh), (Nujol) ν(CN) 2244 (vw), ν(C═C) 1489 (w) cm^{-1}, other bands at 1445 (w), 1440 (m), 1421 (m), 1247 (m), 1237 (m), 1067 (w), 1061 (w), 1017 (m), 1009 (w), 858 (m), 839 (s), 831 (sh), 780 (w), 770 (s), 695 (s) cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 6.16 (s, 5 H, C_5H_5), 7.64 (s, 5 H, Ph); ^{13}C NMR [$(CD_3)_2CO$] δ 94.0 (s, C_5H_5), 112.2, 113.2 (2 × s, CN), 127.1, 130.3, 131.4, 131.7 (4 × s, Ph), 216.7 (s, CO). Compound **9** converted to **10** before other carbons were detected. *Note*: compound **9** must be stored in the dark. Anal. Calcd for $C_{22}H_{10}N_4O_3W$: C, 47.0; H, 1.8; N, 10.0; M, 562. Found: C, 47.5; H, 1.3; N, 10.0; *M* (mass spectrometry), 562.

(b) $W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (10). After 2 days in the dark at room temperature, a solution of $W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$ (400 mg, 0.92 mmol) and $C_2(CN)_4$ (125 mg, 0.98 mmol) in dichloromethane (30 mL) had become orange. Filtration and addition of hexane afforded orange microcrystals of $W\{C[{=}C(CN)_2]CPh{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**10**) (350 mg, 68%): mp >155 °C dec; infrared (CH_2Cl_2) ν(CO) 2046 (s), 1981 (vs, br), (Nujol) ν(CN) 2222 (m), 2210 (m), ν(C═C) 1522 (s) cm^{-1}, other bands at 1440 (m), 1418 (m), 1258 (w), 1248 (w), 1190 (w), 1181 (w), 1170 (w), 1105 (w), 1062 (w), 1050 (m), 1003 (m), 1000 (m), 992 (w), 882 (m), 868 (s), 818 (m), 760 (s), 736 (m), 696 (s), 647 (w), 619 (w) cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 5.91 (s, 5 H, C_5H_5), 7.8 (m, 5 H, Ph); ^{13}C NMR [$(CD_3)_2CO$] δ 77.4 (s, C(1)), 95.7 (s, C_5H_5), 99.8 (s, C(4)), 113.0, 113.3, 113.5, 116.2 (4 × s, CN), 129.8, 130.7, 130.9, 134.9 (4 × s, Ph), 182.8 (s, C(2)), 196.9, 216.8, 217.8 (3 × s, CO), 221.7 (s, C(3)). Anal. Calcd for $C_{22}H_{10}N_4O_3W$: C, 47.0; H, 1.8; N, 10.0; M, 562. Found: C, 46.9; H, 1.4; N, 9.9; M (mass spectrometry), 562. Further crystallization of the mother liquor yielded orange crystals of $W[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](CO)_2(\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (**11**) (ca. 20 mg): mp 175–180 °C; infrared (CH_2Cl_2) ν(CO) 2080 (vs), 2025 (vs), (Nujol) ν(CN) 2232 (s), 2222 (m), ν(C═C) 1586 (s) cm^{-1}, other bands at 3108 (m), 1448 (m), 1420 (m), 1329 (w), 1153 (w), 1078 (w), 1066 (w), 1006 (m), 1003 (sh), 999 (sh), 889 (w), 871 (s), 833 (w), 816 (sh), 812 (m), 772 (s), 697 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.89 (s, 5 H, C_5H_5), 7.48 (s, 5 H, Ph); ^{13}C NMR: ($CDCl_3$) δ 4.7 (s, C(11), 79.4 (s, C(9)), 94.1 (s, C_5H_5), 112.2, 115.2, 116.5, 118.4 (4 × s, CN), 128.7, 129.9, 130.8, 131.5 (4 × s, Ph), 201.1, 203.8 (2 × s, CO), 206.6 (s, C(12)) [C(13) was not detected]. Anal. Calcd for $C_{21}H_{10}N_4O_2W\cdot 0.5C_6N_4$: C, 48.2; H, 1.7; N, 14.1; *M* ($C_{21}H_{10}N_4O_2W$), 534. Found: C, 48.2; H, 1.3; N, 14.0; *M* (mass spectrometry), 534.

(c) $W[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (11). A solution of $W\{C[{=}C(CN)_2]C(Ph){=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**10**) (120 mg, 0.21 mmol) in acetone-d_6 (2 mL) was irradiated (Phillips high-pressure mercury lamp, 125 w) for 25 h until complete conversion (^{1}H NMR) to **11** had occurred. Purification by TLC (silica gel; 1:3 acetone/petroleum ether, boiling range 40–60 °C) and crystallization (acetone/EtOH) gave orange crystals of $W[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](CO)_2(\eta\text{-}C_5H_5)$ (**11**) (70 mg, 62%).

ESR Spectra. The ESR spectrum of the dark green species was measured immediately after solutions of **8** and $C_2(CN)_4$ in benzene were mixed (1:1 ca 25 mmol) in a 2-mm diameter tube and the tube was placed in the ESR cavity. The signal reached maximum intensity ca. 20 min after the solutions were mixed and thereafter decayed within 2 h.

Crystal Structure of $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (11). Data Collection. A crystal, formed as a yellow-orange diamond-shaped plate, was mounted on a glass fibre with epoxy resin. Precession photography that was used for the preliminary work indicated the monoclinic system while the conditions $h + l \neq 2n$ for $h0l$ and $k \neq 2n$ for $0k0$ indicate the space group to be $P2_1/n$.

Lattice parameters at 21 °C were determined by a least-squares fit to the setting angles of 25 independent reflections measured on a four-circle CAD-4 Enraf-Nonius diffractometer employing graphite-monochromated Mo Kα radiation.

Crystal data: $C_{21}H_{10}N_4O_2W.0\text{·}5C_6N_4$: M_r = 598.2; monoclinic, space group $P2_1/n$; a = 12.194 (4) Å, b = 20.858 (5) Å, c = 8.969 (2) Å, β = 98.21 (2)°; U = 2258 Å^3, Z = 4, D_{calcd} = 1.759 g cm^{-3}; $F(000)$ = 1144 electrons; μ(Mo Kα) = 52.29 cm^{-1}.

Intensity data were collected in the range $1.5° \leq \theta \leq 25°$ using a $\omega-(n/3)\theta$ scan where the value of n was optimized by peak analysis and found to be 3. The ω scan angles and horizontal counter apertures employed were $(0.85 + 0.35 \tan \theta)°$ and $(2.10 + 1.00 \tan \theta)$ mm, respectively. Data reduction was performed

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Table III. Valence Angles (deg) in $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (11)

C(2)-W(1)-C(1)	83.8 (3)	C(14)-C(13)-C(12)	121.1 (7)	C(10)-C(9)-W(1)	111.9 (5)
C(9)-W(1)-C(2)	125.2 (3)	C(15)-C(13)-C(14)	117.5 (6)	C(11)-C(9)-W(1)	69.8 (4)
C(11)-W(1)-C(2)	89.2 (3)	N(4)-C(15)-C(13)	177.6 (8)	C(11)-C(9)-C(10)	117.0 (6)
C(12)-W(1)-C(1)	124.8 (3)	C(21)-C(16)-C(11)	122.5 (6)	C(9)-C(11)-W(1)	72.2 (4)
C(12)-W(1)-C(9)	63.7 (3)	C(18)-C(17)-C(16)	120.7 (8)	C(12)-C(11)-C(9)	104.5 (6)
O(1)-C(1)-W(1)	178.9 (8)	C(20)-C(19)-C(18)	119.6 (8)	C(16)-C(11)-C(9)	129.0 (6)
C(7)-C(3)-C(4)	107.4 (7)	C(20)-C(21)-C(16)	120.6 (7)	C(11)-C(12)-W(1)	77.4 (4)
C(6)-C(5)-C(4)	109.6 (7)	C(24)-C(23)-C(22)	119.3 (8)	C(13)-C(12)-C(11)	132.1 (7)
C(6)-C(7)-C(3)	108.1 (7)	C(9)-W(1)-C(1)	81.3 (3)	C(15)-C(13)-C(12)	121.4 (6)
C(8)-C(9)-W(1)	119.9 (6)	C(11)-W(1)-C(1)	87.8 (3)	N(3)-C(14)-C(13)	179.1 (10)
C(10)-C(9)-C(8)	110.6 (6)	C(11)-W(1)-C(9)	38.1 (2)	C(17)-C(16)-C(11)	119.4 (6)
C(11)-C(9)-C(8)	122.1 (6)	C(12)-W(1)-C(2)	83.7 (3)	C(21)-C(16)-C(17)	117.9 (7)
N(2)-C(10)-C(9)	177.2 (8)	C(12)-W(1)-C(11)	38.6 (2)	C(19)-C(18)-C(17)	120.2 (8)
C(12)-C(11)-W(1)	64.0 (4)	O(2)-C(2)-W(1)	178.0 (8)	C(21)-C(20)-C(19)	121.0 (8)
C(16)-C(11)-W(1)	134.0 (5)	C(5)-C(4)-C(3)	107.6 (7)	C(23)-C(22)-N(5)	175.0 (9)
C(16)-C(11)-C(12)	126.0 (6)	C(7)-C(6)-C(5)	107.2 (8)	N(6)-C(24)-C(23)	173.6 (10)
C(13)-C(12)-W(1)	150.4 (5)	C(9)-C(8)-N(1)	177.2 (7)		

Table IV. Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Non-Hydrogen Atoms in $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (11)

	x	*y*	*z*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
W(1)	1594	1694	10304	32	42	40	4	2	3
C(1)	21 (6)	1455 (5)	9375 (9)	43 (4)	97 (6)	61 (5)	19 (5)	0 (4)	−13 (4)
O(1)	−853 (5)	1329 (5)	8880 (8)	48 (4)	198 (9)	84 (5)	14 (5)	−5 (3)	−42 (5)
C(2)	1469 (6)	912 (4)	11589 (9)	51 (4)	63 (5)	60 (5)	6 (4)	7 (4)	0 (4)
O(2)	1397 (6)	485 (3)	12342 (8)	110 (5)	77 (4)	101 (5)	49 (4)	25 (4)	4 (4)
C(3)	2685 (6)	2532 (4)	11339 (10)	51 (4)	59 (5)	83 (6)	−28 (4)	11 (4)	−6 (3)
C(4)	1792 (7)	2812 (4)	10373 (8)	81 (5)	47 (4)	53 (4)	−6 (3)	11 (4)	−1 (4)
C(5)	833 (7)	2655 (4)	10922 (9)	55 (4)	61 (5)	64 (5)	−6 (4)	5 (4)	25 (4)
C(6)	1085 (7)	2286 (4)	12234 (9)	71 (5)	70 (5)	53 (5)	2 (4)	22 (4)	14 (4)
C(7)	2235 (7)	2209 (4)	12493 (9)	72 (5)	70 (5)	56 (5)	−15 (4)	−17 (4)	17 (4)
N(1)	154 (7)	1782 (3)	5746 (9)	63 (5)	73 (5)	62 (5)	5 (3)	−12 (4)	11 (4)
C(8)	911 (7)	1722 (3)	6676 (8)	53 (4)	39 (4)	47 (4)	1 (3)	−1 (4)	1 (3)
C(9)	1847 (6)	1681 (3)	7828 (8)	41 (4)	35 (3)	48 (4)	2 (3)	5 (3)	−2 (3)
C(10)	2704 (6)	2123 (3)	7530 (8)	44 (4)	41 (4)	47 (4)	1 (3)	9 (3)	−1 (3)
N(2)	3345 (6)	2487 (3)	7272 (9)	73 (5)	57 (4)	93 (6)	−5 (4)	30 (4)	−15 (4)
C(11)	2211 (5)	1066 (3)	8559 (8)	35 (3)	38 (4)	41 (4)	5 (3)	0 (3)	1 (3)
C(12)	3020 (6)	1246 (3)	9818 (7)	46 (4)	39 (3)	44 (4)	5 (3)	4 (3)	7 (3)
C(13)	4103 (6)	1092 (3)	10200 (8)	40 (4)	57 (4)	41 (4)	−1 (3)	0 (3)	10 (3)
C(14)	4718 (6)	1309 (4)	11581 (10)	40 (4)	86 (6)	51 (5)	4 (4)	−1 (4)	8 (4)
N(3)	5193 (7)	1482 (5)	12684 (10)	67 (5)	129 (7)	67 (5)	−17 (5)	−15 (5)	4 (5)
C(15)	4674 (6)	724 (4)	9232 (9)	45 (4)	76 (6)	43 (4)	12 (4)	2 (3)	16 (4)
N(4)	5105 (7)	420 (4)	8415 (9)	68 (5)	103 (6)	59 (5)	7 (4)	11 (4)	33 (5)
C(16)	1959 (5)	407 (3)	8025 (8)	38 (3)	35 (3)	52 (4)	−2 (3)	7 (3)	−1 (3)
C(17)	2298 (7)	−113 (3)	8980 (10)	64 (5)	38 (4)	66 (5)	11 (4)	5 (4)	10 (4)
C(18)	2105 (8)	−735 (4)	8492 (13)	69 (6)	35 (5)	106 (8)	7 (5)	17 (6)	11 (4)
C(19)	1573 (7)	−856 (4)	7053 (13)	69 (5)	36 (4)	105 (8)	−11 (5)	24 (5)	−3 (4)
C(20)	1262 (7)	−355 (4)	6107 (11)	56 (5)	53 (4)	85 (7)	−17 (4)	−6 (5)	−1 (4)
C(21)	1473 (5)	273 (3)	6568 (9)	44 (4)	42 (4)	65 (5)	−1 (3)	−5 (4)	3 (3)
N(5)	3467 (6)	1091 (3)	5165 (9)	75 (5)	58 (4)	82 (5)	2 (4)	0 (4)	7 (4)
C(22)	4128 (7)	720 (4)	5178 (9)	65 (4)	52 (4)	62 (5)	5 (4)	10 (4)	19 (4)
C(23)	5057 (10)	282 (4)	5221 (11)	124 (8)	65 (5)	67 (6)	12 (5)	36 (6)	23 (6)
C(24)	6189 (8)	519 (4)	5736 (11)	67 (5)	64 (5)	88 (6)	8 (4)	24 (5)	−14 (4)
N(6)	7018 (7)	742 (4)	6213 (10)	70 (5)	74 (5)	96 (6)	12 (4)	5 (4)	−1 (4)

by using the program SUSCAD[43] which also applied the Lorentz and polarization corrections. In all 3661 reflections were collected of which 880 with $I < 2.5\sigma(I)$ were omitted leaving 2781 which were used in all subsequent calculations.

Structure Solution and Refinement. The tungsten atom position was determined by Harker analysis of a three-dimensional Patterson synthesis, and all other non-hydrogen atoms were located from subsequent Fourier maps. Hydrogen atoms were included at calculated sites (C–H = 0.95 Å) with group temperature factors while anisotropic thermal parameters were employed for all other atoms. Blocked-matrix least-squares techniques were used to refine all positional and thermal parameters. A weighting scheme was applied and refined, converging at $w = 0.58/(\sigma^2 F_o + 0.0034F_o^2)$, while refinement converged with all shifts less than 1σ, with $R = 0.0389$ and $R_w = 0.0394$ [$R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = \sum(|F_o| - |F_c|)w^{1/2}/\sum(|F_o|w^{1/2})$]. At this stage the maximum residual peak (height 0.56 e Å^{-3}) remaining in a final difference map was located about 0.9 Å from the tungsten. All calculations were performed by using the SHELX[41] system of programs.

Table I lists non-hydrogen atom coordinates, and selected bond distances and angles are collected in Tables II and III.

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Supplementary Material Available: Tables of observed and calculated structure factors and of positional and thermal parameters for hydrogen atoms in $W(CO)_2[\eta^3\text{-}C(CN)_2CPhC{=}C(CN)_2](\eta\text{-}C_5H_5)\cdot 0.5C_2(CN)_4$ (11) (17 pages). Ordering information is given on any current masthead page.

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(43) Programmes used included: SUSCAD, data reduction program for the CAD-4 diffractometer, University of Sydney, 1976; SHELX, program for crystal structure determination, G. M. Sheldrick, University of Cambridge, 1976.